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Hybrid One-Dimensional 15-Crown-5-ether-uranyl-selenate Polymers in $[K@(C_{10}H_{20}O_5)][(UO_2)(SeO_4)(HSeO_4)(H_2O)]$: Synthesis and Characterization

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Keywords: Uranyl selenate; Crown ether; Potassium; Topology; Crystal structure

Abstract. The hybrid organic-inorganic uranyl selenate, $[K@(C_{10}H_{20}O_5)][(UO_2)(SeO_4)(HSeO_4)(H_2O)]$ (**I**), was prepared by isothermal evaporation from aqueous solutions. The crystal structure of **I** [orthorhombic, *Pnma*, a = 15.386(3), b = 10.771(2), c = 13.239(3) Å, V = 2194.0(7) Å^3, Z = 4, R_1 = 0.042] is based upon complex 15-crown-5-ether-uranyl-selenate polymeric units consisting of uranyl selenate chains decorated by $[K@(15\text{-crown-5})]^+$ complexes via strong ionic K^+–O bonds. The 1D hybrid units are packed in a parquetted-like fashion and connected to each other by hydrogen bonds and residual van der Waals interactions.

Introduction

Mixed organic-inorganic compounds containing hexavalent uranium atoms, especially uranyl selenates, are of particular interest due to the wide variety of chemical compositions and types of structural arrangements.[1] The U^{6+} cations in these compounds generally occur as linear uranyl ions, $[O=U=O]^{2+}$, coordinated in the equatorial plane by 4, 5, or 6 additional anions. As a result of strongly asymmetrical distribution of bond strength inside uranium polyhedra, their polymerization usually results in formation of low-dimensional structural topologies with the significant prevalence of layered structures.[2] However, one-dimensional units are also common and, at least for uranyl selenates, can be tentatively divided into two structural types. In the most common case, the uranyl-based chains are arranged into pseudo 2D layers, in which they are linked to each other by relatively strong hydrogen bonds due to the presence of either hydroxyl groups or H_2O molecules.[2,3] The negatively charged pseudo-layers are usually separated by cationic interlayer subunits of various complexity. Similar type of 1D units arrangement is also quite common for other uranyl oxoanion systems, such as sulfates,[4] chromates,[5] or molybdates.[6] Another more specific and rare type of structural arrangements is observed in structures with rather sophisticated architecture that involve not only hydrogen bonding but strong covalent and ionic interactions to combine both organic and inorganic units.

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Recently, we have reported on the novel uranyl selenate based upon the uranyl selenate-nitrate polymeric chains linked to the $[K@(18\text{-crown-6})(H_2O)]^+$ complexes by the K–O bonds.[7] The hybrid organic-inorganic units are linked to each other by secondary and weak bonds only. In general, the presence of K^+ cations in uranyl selenate aqueous solutions sometimes result in quite unexpected inorganic topologies such as uranyl selenate nanotubules.[8] Along this direction, several synthetic experiments were performed using smaller-sized 15-crown-5 ether molecules co-crystallizing with K^+ and uranyl selenates in aqueous solutions. Herein we report on the synthesis, crystal structure, and spectroscopic investigations of the new compound $[K@(C_{10}H_{20}O_5)][(UO_2)(SeO_4)(HSeO_4)(H_2O)]$ (**I**) that demonstrates a novel type of structural association of uranyl oxysalt one-dimensional units with $[K@(15\text{-crown-5-ether})]^+$ complexes.

Results and Discussion

Compound **I** was prepared by isothermal evaporation from 2 mL of an aqueous solution of uranyl nitrate hexahydrate, selenic acid, potassium oxalate, and 15-crown-5 ether at room temperature conditions. The crystals of **I** formed from the mixture after 5 d. The structure of **I** was analyzed by single-crystal X-ray diffraction and IR spectroscopy. The band assignment shows that the vibrational spectroscopic data are in a good agreement with the chemical composition and the results of single-crystal X-ray diffraction study.

Single-crystal X-ray diffraction analysis reveals that **I** crystallize in the orthorhombic system (Figure 1). The unit cell of **I** contains one symmetrically independent U atom occupying special crystallographic position locating on the mirror plane with two short U^{6+}=O^{2-} bonds [1.750(8) and 1.751(8) Å] forming an approximately linear UO_2^{2+} uranyl ion (Ur). The

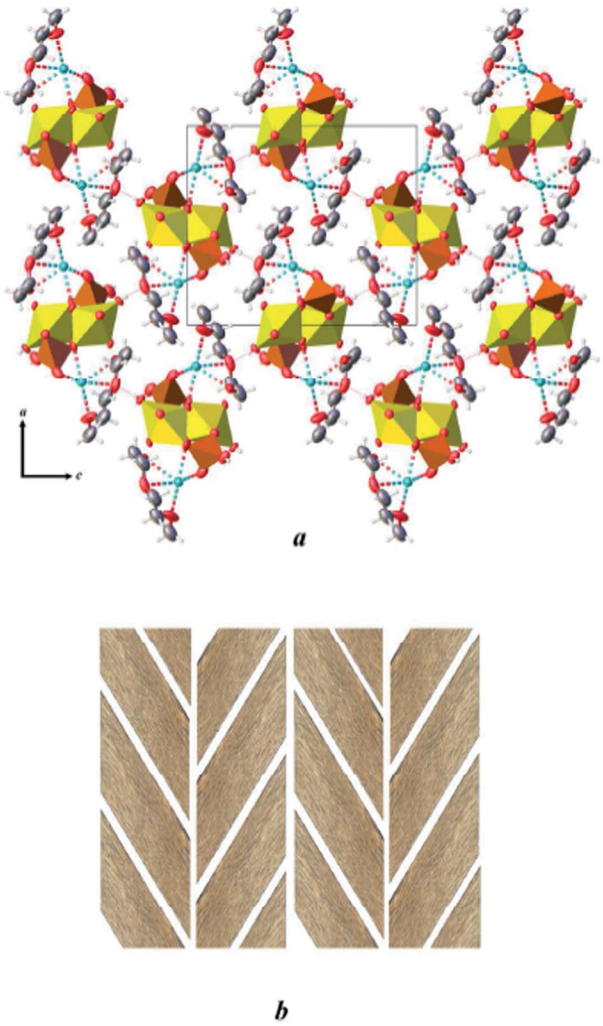

Figure 1. Crystal structure of [K@(15-crown-5)][$(UO_2)(SeO_4)(HSeO_4)(H_2O)$] (**I**) (a). Legend: U polyhedra = yellow, Se tetrahedra = orange, K atoms = light blue, O atoms = red, C atoms = grey, N atoms = blue. Scheme of the 1D hybrid units arrangement in a parquetted-like fashion (b).

$U(1)O_2^{2+}$ cation is coordinated by four oxygen atoms [U(1)–O_{eq} = 2.360(5)–2.394(6) Å] that belong to the selenate oxyanions and one oxygen atom of an H_2O molecule [U(1)–H_2O(7) = 2.485(8) Å] arranged in the equatorial plane of the $Ur(1)O_5$ pentagonal bipyramid. One symmetrically non-equivalent Se^{6+} atom occupies general position and is tetrahedrally coordinated by four O^{2-} atoms (<Se–O> = 1.630 Å). The SeO_4 tetrahedra are bidentate, sharing two vertices with two adjacent uranium polyhedra each. One of the non-bridging vertices of the selenate group forms the K–O bond. The U and Se coordination polyhedra polymerize by sharing common oxygen atoms to form one-dimensional uranyl selenate $[(UO_2)(SeO_4)(HSeO_4)(H_2O)]^-$ anionic chains (Figure 2). Its topology corresponds to the black-and-white graph shown in Figure 2c.[9] This topology is one of the most prevalent among the one-dimensional uranyl compounds and has been observed in both inorganic and organic-inorganic hybrid compounds

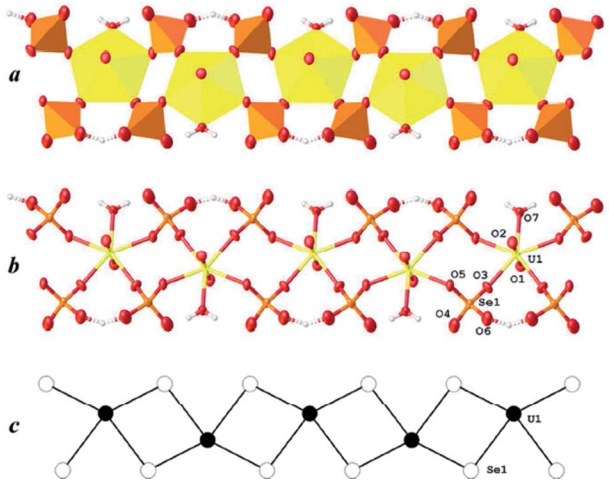

Figure 2. Uranyl selenate 1D unit in **I** shown in polyhedra (a) and ellipsoids (50% probability level) (b) and graphical representation of the infinite chain in **I** (c). Legend: U atoms and polyhedra = yellow, Se atoms and tetrahedra = orange, O atoms = red; H atoms = white.

[see, for example, $Zn[(UO_2)(SeO_4)_2(H_2O)](H_2O)_4$[3d] and $(CH_3NH_3)_2[(UO_2)(SeO_4)_2(H_2O)](H_2O)$[3i]]

The negative charge of the 1D inorganic units is compensated by the asymmetric $[K@(15\text{-crown-5})]^+$ complexes located on both sides of the inorganic chains. In general, the K atom is coordinated by eight oxygen atoms [K–O = 2.733(11)–3.018(8) Å] (Figure 3b). Since the K^+ ion size is larger than can be accommodated by the 15-crown-5 molecule, the K^+ cation is located 1.85(1) Å above the center of the crown ring and forms five K–O bonds to its oxygen atoms. Another three K–O bonds are accounted for the oxygen atoms of the uranyl selenate chain: two equivalent K–O4 bonds to the terminal O4 atoms of selenate tetrahedra and one K–O2 bond to the uranyl O2 atom (this type of coordination is typical for K-containing uranyl selenates[10]). It is worthy to note there is a very short [2.363(9) Å] O6–O6 contact between the O6 atoms of the neighboring selenate tetrahedra, which corresponds to a symmetrical hydrogen bond. However, the asymmetry of the O6–H···O6 arrangement cannot be excluded, but, due to the presence of a mirror plane between the O6 atoms, such an arrangement should be disordered. Additional evidence in

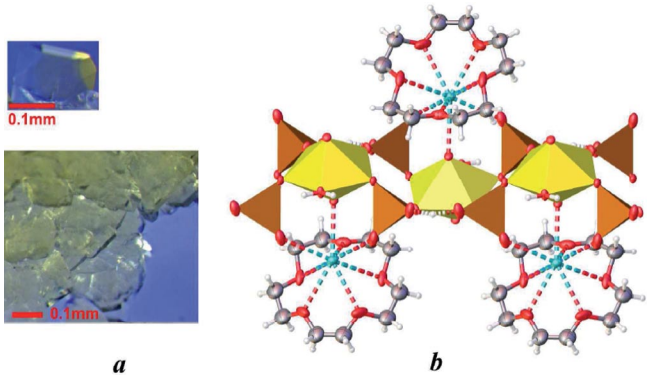

Figure 3. Crystals of **I** (a) and coordination of K atoms in the structure of **I** (b).

favor for this hypothesis comes from the existence of vibration bands at 711 and 736 cm^{-1} in the infra-red spectra (Figure 4), which supports the observation that compounds having stretching frequencies around 720 cm^{-1} are the candidates for the single potential minima.[11]

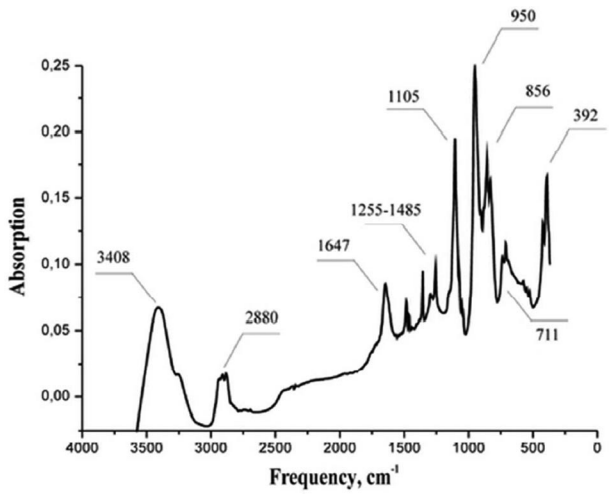

Figure 4. IR spectra of **I**.

The mutual arrangement of one-dimensional uranyl selenate polymeric chain and $[K@(15\text{-crown-5})]^+$ complexes in the structure of **I** is unique and was not observed previously. By forming relatively strong ionic K^+–O bonds, uranyl selenate units, and crown ether molecules form complex $\{[K@(15\text{-crown-5})][(UO_2)(SeO_4)(HSeO_4)(H_2O)]\}$ rods packed together in a parquette-like arrangement and linked by weak van der Waals and hydrogen bonds only.

Therefore, the title compound reported herein provides a novel and previously unreported type of a hybrid one-dimensional organic-inorganic polymeric arrangement in uranyl oxysalts, where interaction between inorganic and organic subunits is mediated by ionic K^+–O bonds.

Experimental Section

Synthesis of I: A mixture of $(UO_2)(NO_3)_2{\cdot}6H_2O$ (0.021 g, Vekton, 99 %), $K_2C_2O_4$ (0.008 g, Vekton, 98 %), $C_{10}H_{20}O_5$ (0.011 g, Sigma-Aldrich, 98 %), H_2SeO_4 (40 wt % in H_2O, 0.3 mL, Sigma-Aldrich, 99.95 %) and deionized distil water (2 mL) was stirred to homogenization and left in a watch glass at a room temperature. After 3 d yellowish-green prismatic crystals were recovered from the solution.

X-ray Crystallography: Crystal of **I** was mounted on thin glass fiber for X-ray diffraction analysis, which was carried out with a Bruker SMART single-crystal X-ray diffractometer equipped with an APEX II CCD planar detector operated with Mo-K_α radiation at 50 kV and 40 mA. More than a hemisphere of X-ray diffraction data (θ_{max} = 27.50°) were collected at 210 K for the crystal with frame widths of 0.5° in ω, and exposition of 40 s spent per each frame. Data were integrated and corrected for background, Lorentz, and polarization effects using an empirical spherical model by means of the Bruker programs APEX2 and XPREP. Absorption correction was applied using the *SADABS* program.[12] The unit cell parameters of **I** were determined and refined by the least-squares techniques on the basis of 23398 reflections with 2θ in the range of 4.06–55.00°. From the systematic absences and statistics of reflection distribution, the space group *Pnma* was determined. The structure was solved by direct methods and refined to R_1 = 0.042 (wR_2 = 0.112) for 2047 reflections with $|F_o| \geq 4\sigma F$ using the *SHELXL*-97 program incorporated in the OLEX2 program package.[13] The final model included coordinates and anisotropic displacement parameters for all non-hydrogen atoms. The carbon-bound hydrogen atoms were placed in calculated positions and were included in the refinement in the "riding" model approximation, with U_{iso}(H) set to 1.2U_{eq}(C) and C–H 0.97 Å. Positions of hydrogen atoms of H_2O molecule and OH^- group were localized from difference Fourier maps and kept fixed during refinement.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-1021738 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

IR Spectroscopy: The IR spectra of **I** were recorded using KBr pellets with the Bruker Vertex 70 spectrometer in the region 4000–300 cm^{-1}. IR spectra of **I** shows characteristic absorption bands at 860–390 cm^{-1} (392, 422, 524, 547, 611, and 831 cm^{-1}) due to the presence of $[SeO_4]^{2-}$ anions, these bands can be attributed to the stretches of the Se–O bonds. Strong bands at 711, 736 and 1105 cm^{-1} are assigned as the characteristic Se–OH stretch of $[HSeO_4]^-$. The bands at 950–860 cm^{-1} (in particular 856, 906, and 960 cm^{-1}) are due to the vibrations of the $(UO_2)^{2+}$ cations.[14] It should be noted that characteristic vibrations of the oxoselenate groups and uranyl ions overlap, so they cannot be clearly separated without structure-based calculations.[15] The diffuse bands in the range of 3400–3200 cm^{-1} (3258 and 3408 cm^{-1}) and individual peaks (2910, 2934, and 1647 cm^{-1}) correspond to the O–H stretching vibrations of water molecules. A series of weak bands in the range 1650–1250 cm^{-1} (1255, 1283, 1296, 1440, 1462, and 1483 cm^{-1}) and several individual peaks (2910 and 2934 cm^{-1}) are the characteristic bands for the stretching and deformation vibrations of C–H bonds in the crown ether molecules. Two weak bands at 1342 and 1355 cm^{-1} are characteristic for the stretching vibrations of C–C, and diffuse band of irregular shape with a maximum at 2883 cm^{-1} is characteristic of the stretching vibrations of C–O in the crown ether molecules.

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